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Article

Selective Activation of Benzylic Carbon−Hydrogen Bonds of Toluenes with Rhodium(III) Porphyrin Methyl: Scope and Mechanism

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Toluenes underwent selective benzylic carbon−hydrogen bond activation (BnCHA) with rhodium(III) porphyrin methyl. The *ortho*-, *meta*-, and *para*-substituted toluenes yielded the corresponding rhodium porphyrin benzyls in high yields in solvent-free conditions as well as in benzene solvent. Mechanistically, Rh(ttp)Me likely undergoes a σ-bond metathesis pathway. The small value of the kinetic isotope effect (2.7) indicates a bent transition state. The negative slope (−1.1) of the linear free energy relationship Hammett plot supports that the benzylic carbon builds up a positive charge in the transition state.

Introduction

The carbon−hydrogen bond activation (CHA) using transition metal complexes plays an important role in converting saturated hydrocarbons to functionalized organic compounds.[1] Late transition metal complexes are more appealing than their early transition metal counterparts due to the broader functional group compatibilities.[2] Therefore, both exploratory and mechanistic studies would aid in discovering the rich chemistry of high-valent late transition metal complexes in bond activations.

For CHA by high-valent late transition metal complex, a few mechanistic possibilities exist, such as oxidative addition (OA),[3] σ-bond metathesis (SBM),[4] and (base-promoted) heterolysis.[5] However, the OA and SBM are often not easily distinguished for rhodium(III) and iridium(III) complexes. The successful isolation of high-valent metal(V) intermediates in the Si−H activation has firmly established the OA pathway in some cases.[3]

We have been interested in the chemistries of alkyl,[6] aryl,[7] benzylic,[8] and aldehydic[9] carbon−hydrogen bond activations and silicon−hydrogen activation of silanes[10] by both rhodium(III) and iridium(III) porphyrin chlorides.[11] These types of metalloporphyrins are unique due to the apparent steric difficulties of *cis*-coordination of a substrate to the five-coordinate metalloporphyrin complex in the course of bond activation and the relative electronic inaccessibility of an oxidative addition intermediate that requires a formal M(V) oxidation state. Previously, we have also discovered the base-promoted selective benzylic (Bn) CHA of toluenes by rhodium(III) tetrakis(4-tolylporphyrin) chloride (Rh^{III}(ttp)Cl).[8] To gain further mechanistic understanding of the BnCHA of toluenes by metalloporphyrins, studies have been extended to Rh^{III}(ttp)Me bearing a nonionizable Rh-Me group. We now report the synthetic results and mechanistic investigation revealing a bent transition state via SBM.

Results and Discussion

Rh(ttp)Me reacted with toluene in solvent-free conditions successfully and selectively in BnCHA at 150 °C in 1 day to give Rh(ttp)Bn in 91% yield (eq 1, Table 1, entry 2), while no reaction occurred at 120 °C in 2 days (Table 1, entry 1). In contrast with the nonselective reaction with Rh(ttp)Cl, no aryl CHA product was observed.[8] The BnCHA also proceeded smoothly in benzene solvent using 10 equiv of toluene but with slightly lower efficiency. A longer reaction time of 4 days was required, and slightly lower product yield of 69% was obtained (Table 1, entry 3). The reaction was faster at 200 °C and gave a high product yield of 91% (Table 1, entry 4). Thus Rh(ttp)Me is less reactive but more selective than Rh(ttp)Cl. Methane was also identified and formed in 76%

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Table 1. Temperature Effect on CHA of Toluene with Rh(ttp)Me

$$\mathrm{Rh(ttp)Me} \xrightarrow[\text{temp, time, } N_2]{PhCH_3} \mathrm{Rh(ttp)Bn} \qquad (1)$$

entry	temp/°C	time	yield/%
1	120	2 d	no rxn[a]
2	150	1 d	91
3	150	4 d	69[b]
4	200	2 h	91

[a] Rh(ttp)Me recovered in 92%. [b] 10 equiv of toluene in benzene, CH_4 formed in 76%.

Table 2. Base Effect on CHA of Toluene

$$\mathrm{Rh(ttp)Me} + PhCH_3 \xrightarrow[150°C,\ 6\ h,\ N_2]{10\ \text{equiv of base}} \mathrm{Rh(ttp)Bn} \qquad (2)$$

entry	base	yield Rh(ttp)Bn/%	recovered yield of Rh(ttp)Me/%	total yield/%
1	none	80	12	92
2	K_2CO_3	33	55	88
3	K_3PO_4	14	72	86
4	Ph_3P[a]	0	50[b]	50[b]

[a] 3 equiv was used. [b] (Ph_3P)Rh(ttp)Me was obtained.

Table 3. Scope of Substrate

$$\mathrm{Rh(ttp)Me} + \text{FG-BnH} \xrightarrow[150°C,\ N_2]{} \text{Rh(ttp)Bn-FG} \qquad (3)$$

entry	FG	time	yield (%)
1	4-Me	7 h	**1a** (76)
2	4-^{t}Bu	4 h	**1b** (82)
3	4-H	1 d	**1c** (91)
4	4-F	15 d	**1d** (48[a])
5	4-Cl	1 d	**1e** (69)
6	4-CF_3	4 d	**1f** (83)
7	4-CN	17 d	**1g** (71)
8	3-Me	3 d	**1h** (77)
9	2-Me	4 d	**1i** (79)

[a] Rh(ttp)Me dissolved poorly in 4-fluorotoluene and was recovered in 24%.

when the reaction was carried out in a sealed NMR tube in benzene-d_6 (Table 1, entry 3; see also SI).

Base Effect. With the reported base-promoted selective BnCHA by Rh(ttp)Cl at 120 °C,[8] we thus explored the effect of added bases. The control experiment was carried out in 6 h. Rh(ttp)Me did not react completely and was recovered in 12% yield together with Rh(ttp)Bn formed in 80% yield (eq 2, Table 2, entry 1). When 10 equiv of K_2CO_3 was added, only a 33% yield of Rh(ttp)Bn was isolated and a 55% yield of Rh(ttp)Me recovered (Table 2, entry 2). Similarly, the addition of 10 equiv of K_3PO_4 gave a 14% yield of Rh(ttp)Bn and a 72% yield of recovered Rh(ttp)Me (Table 2, entry 3). Therefore, Rh(ttp)Bn was formed in lower yields and more slowly in the presence of bases. It is likely that a base can coordinate to Rh(ttp)Me to retard the BnCHA reaction, as the Rh center is also Lewis acidic. Indeed, the addition of the coordinating Ph_3P ligand did not produce any BnCHA product but yielded only (Ph_3P)Rh(ttp)Me in 50% yield (Table 2, entry 4) and shut down the CHA reaction completely.

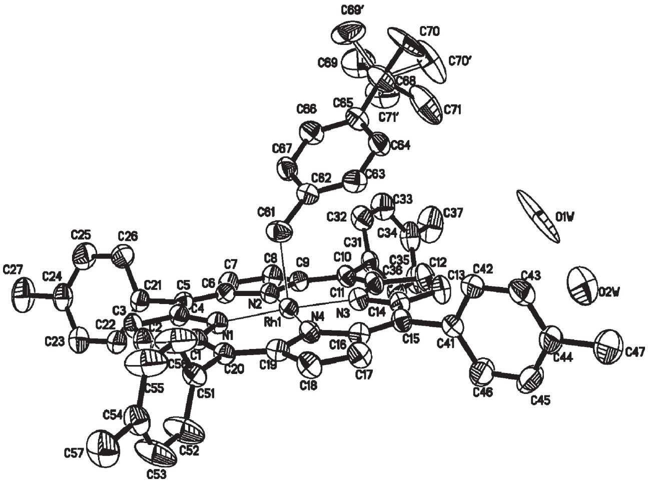


Figure 1. ORTEP drawing of Rh(ttp)Bn(4-^{t}Bu) (**1b**) (30% probability displacement ellipsoids).

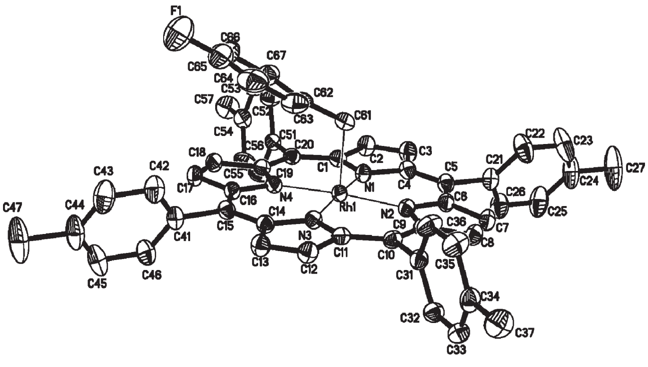


Figure 2. ORTEP drawing of Rh(ttp)Bn(4-F) (**1d**) (30% probability displacement ellipsoids).

Table 4. Selected Bond Lengths (Å) and Max. Deviation of Rh(ttp)Bn(4-^{t}Bu) and Rh(ttp)Bn(4-F)

entry	FG	Rh−C_α length/Å	Rh−N_{av}/Å	max. deviation from the least-squares plane/Å
1	4-^{t}Bu, **1b**	2.085(5)	2.019	0.162(5)
2	4-F, **1d**	2.064(3)	2.024	0.132(4)

Scope of Substrate. To examine the substrate scope of toluene, the optimized reaction conditions were applied to various substituted toluenes. Generally, high yields of rhodium porphyrin benzyls were obtained (Table 3, eq 3). Electron-rich toluenes gave faster reaction rates than electron-poor toluenes (Table 3, entries 1−7). More sterically hindered *ortho*- and *meta*-xylene were also applicable, but the reactions required longer times (Table 3, entries 8 and 9).

X-ray Structures. Figures 1 and 2 show the X-ray structures of Rh(ttp)Bn(4-^{t}Bu) and Rh(ttp)Bn(4-F). Table 4 lists some selected bond lengths and maximum deviations of the core atoms and rhodium from the 24-atom least-squares planes of Rh(ttp)Bn(4-^{t}Bu) and Rh(ttp)Bn(4-F). The Rh−C_α bond lengths of Rh(ttp)Bn(4-^{t}Bu) and Rh(ttp)Bn(4-F) are similar and are 2.085(5) and 2.064(3) Å, respectively

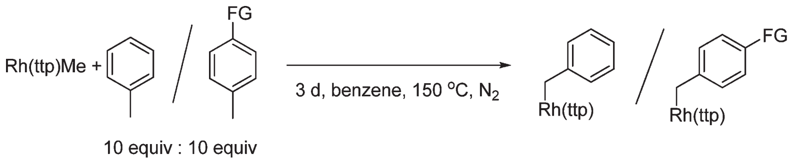
Table 5. Temperature-Dependent Kinetic Isotope Effect of BnCHA

$$\underset{1\ :\ 1}{\mathrm{Rh(ttp)Me + C_6H_5CH_3/C_6D_5CD_3}} \xrightarrow[\text{temp, N}_2]{} \mathrm{Rh(ttp)Bn/Rh(ttp)Bn}\text{-}d_7 \qquad (4)$$

entry	temp/°C	time	$(k_H/k_D)_{obs}$[a]
1	150	1 d	2.7 ± 0.1
2	200	2.5 h	2.8 ± 0.1

[a] Determined by ^{1}H NMR.

Table 6. Competition Experiments of BnCHA



(5)

entry	*p*-FG	σ_p[a]	yield of Rh(ttp)Bn-FG/%	yield of Rh(ttp)Bn/%	log $k(H_{FG}/H_H)$
1	Me	−0.14	59	21	0.45
2	^{t}Bu	−0.15	65	23	0.45
3	F	0.15	49	35	0.16
4	Cl	0.34	32	50	−0.19
5	CF_3	0.53	25	47	−0.28

[a] σ_p: *para*-substituent constant.

(Table 4, entries 1 and 2). The average Rh−N bond lengths in Rh(ttp)Bn(4-^{t}Bu) and Rh(ttp)Bn(4-F) do not have any significant difference, which are 2.019 and 2.024 Å, respectively (Table 4, entries 1 and 2). On the other hand, the substituted benzyls do not cause a large distortion from planarity of the rhodium porphyrin complexes (Table 4, entries 1 and 2).

Kinetic Isotope Effect. The observed kinetic isotope effects $(k_H/k_D)_{obs}$ for the BnCHA of toluene with Rh(ttp)Me were measured by competition experiments with an equimolar mixture of solvent toluene and toluene-d_8. $(k_H/k_D)_{obs}$ were measured to be 2.7 and 2.8 at 150 and 200 °C, respectively (eq 4, Table 5, entries 1 and 2). Since Rh(ttp)Bn did not exchange with toluene-d_8 under the same reaction conditions, the measured values are truly kinetic ones. Therefore, the Bn−H bond cleavage occurs at the rate-limiting step. The nearly identical KIEs suggest little change in Arrhenius behavior[12] and the same reaction mechanism at both temperatures. The small values further indicate a bent transition state in the benzylic C−H cleavage rate-limiting step.

Hammett Studies. To gain some mechanistic understandings of the electronic effect of BnCHA, the Hammett plot was constructed from a series of competition experiments using an equimolar mixture of 4-substituted (FG) toluene and toluene in the reaction with Rh(ttp)Me at 150 °C in 3 days in benzene (eq 5, Table 6). Since Rh(ttp)Bn did not undergo any exchange with 4-FG-BnH, the ratios are kinetic ones. Figure 3 shows that the linear free energy relationship was observed from the Hammett plot using the substituent constant σ_p.[13] As the para substituent becomes more electron-rich, the rate of reaction increases. The plot of log $k(H_{FG}/H_H)$ against σ_p values yields the ρ value of −1.14. Therefore, in the bent transition state, a positive charge buildup occurs on the benzylic carbon.[14] In addition, the linear free energy relationship in the Hammett plot suggests that any prior coordination of the benzylic C−H to the rhodium center unlikely occurs to a significant extent with a change of substituent to affect the rate.[9b]

Proposed Mechanism. Rh(ttp)Me can in principle undergo homolysis to give Rh^{II}(ttp) and methyl radicals or heterolysis into Rh(ttp)$^+$/Me$^-$ or Rh(ttp)$^-$/Me$^+$. The rate of formation of Rh^{II}(ttp) and Me radical by homolysis is too slow to account for the reaction rate, due to the strong Rh−CH$_3$ bond (about 57 kcal/mol).[6,15] Likewise, heterolysis is also unlikely, especially in a nonpolar solvent.[6] The remaining possibility of classical oxidative addition or SBM reported in many CHA reactions[3,4] is experimentally very difficult to distinguish, unless a stable intermediate is isolated. In this porphyrin system, an OA demands a Rh(V) intermediate complex, which is less common. Furthermore the sterics of a Rh porphyrin complex with three *cis* substituents are highly unfavorable to further argue against the OA. We therefore favor that the BnCHA of toluene with Rh(ttp)Me undergoes SBM to give Rh(ttp)Bn (Scheme 1).

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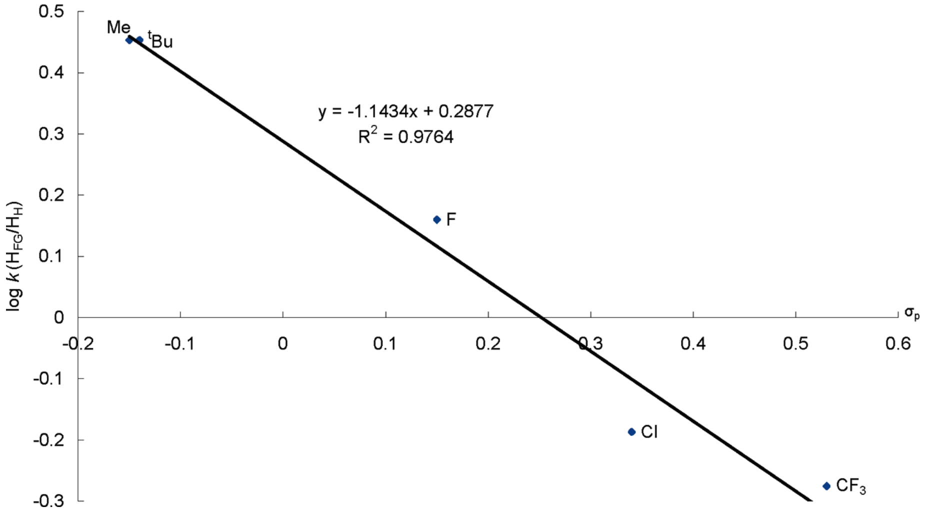
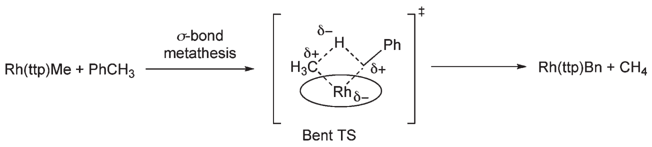


Figure 3. Hammett plot of BnCHA of toluene with Rh(ttp)Me.

Scheme 1. BnCHA of Toluene with Rh(ttp)Me



Many transition metal complexes have been exploited to break C−H bonds by electrophilic activation.[16] For example, $(H_2O)Pt(II)Cl_2$ and $(HSO_4)(SO_4)Au(III)$ reacted with methane, and the Pt and Au centers are both also highly electrophilic.[16d,17] While the reaction between the cationic $[Cp^*(PMe_3)IrMe]^+$ complex with methane is presumed to be promoted by electrophilic C−H activation,[18] Ess et al. have reported recently that the C−H bond cleavage in the $[Cp(PH_3)Ir(Me)\text{-}CH_4]^+$ system is not so electrophilic by theoretical calculation, in contrast to the ground-state cationic nature of the complex.[14a] A change of polarity in the ground state and the transition state of the metal complexes can occur.[14a,19] Experimental studies of the polarity and extent of polarity of bond activation with transition metal complexes will be fruitful for both fundamental understandings and enhancement of reactivity.

In this BnCHA system with Rh(ttp)Me, the polarity reverse of Rh−Me likely occurs in the transition state since a Rh−C is commonly viewed to be a polar covalent bond with the rhodium center bearing the positive charge.[14a,20,21] The nature and direction of the overall charge transfer in carbon−hydrogen bond activation have been reported by Ess et al.[14a] They also computed the Hammett plots of BnCHA in selected metal complexes, which indicate that the benzylic hydrogens can transfer in a hydric, protic, or hydrogen atom like manner depending on the metal complexes. The nucleophilic susbstitution reactions of Rh(ttp)Me with K_2CO_3[22] and the intramolecular ether formation of Rh porphyrin hydroxylalkyl added with base[23] support the electrophilic nature of the carbon α to Rh in the transition states. Likewise, the measured ρ value of -1.14 from the Hammett studies supports that the benzylic C−H bond cleaves as a hydric-like hydrogen in the transition state with the corresponding Rh−Me carbon as an electrophilic center. This demonstrated electronic effect in carbon−hydrogen bond activation would hopefully aid the choice of reagent and design of porphyrin ligand to facilitate the functionalization of Rh−alkyl bonds.

Conclusion

In summary, we have discovered a selective and functional group compatible benzylic CHA of toluenes with Rh(ttp)Me. Rh(ttp)Me undergoes a polar SBM pathway with a positive charge buildup on the benzylic carbon occurring in the bent transition state.

Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Benzene and toluene were distilled from sodium. Thin-layer chromatography was performed on precoated silica gel 60 F_{254}

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plates. Silica gel (Merck, 70−230 mesh) was used for column chromatography.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 at 300 and 75 MHz, respectively. Chemical shifts were referenced with the residual solvent protons in C_6D_6 (δ = 7.15 ppm), $CDCl_3$ (δ = 7.26 ppm), or tetramethylsilane (δ = 0.00 ppm) in ^{1}H NMR spectra and $CDCl_3$ (δ = 77.16 ppm) in ^{13}C NMR spectra as the internal standards. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. Coupling constants (J) were reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Thermo-Finnigan MAT 95 XL mass spectrometer. Fast atom bombardment spectra were performed with 3-nitrobenzyl alcohol (NBA) as the matrix. All samples for combustion analyses were recrystallized from CH_2Cl_2/MeOH and vacuum-dried at room temperature for at least 2 days before submission.

The synthesis of Rh(ttp)Me followed a literature method.[20]

General Procedure for Reactions of Rh(ttp)Me with Toluene at Various Temperature and Benzene. At 120 °C. Rh(ttp)Me (20 mg, 0.025 mmol) and toluene (1.5 mL) were degassed in a Teflon-stoppered tube covered by aluminum foil and heated at 120 °C under N_2 for 2 days. No reaction occurred.

At 150 °C. Rh(ttp)Me (20 mg, 0.025 mmol) and toluene (1.5 mL) were degassed in a Teflon-stoppered tube covered by aluminum foil and heated at 150 °C under N_2 for 1 day. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give Rh(ttp)Bn[9a] **1c** (20 mg, 0.023 mmol, 91%).

At 150 °C with Benzene. Rh(ttp)Me (20 mg, 0.025 mmol) and toluene (27 μL) with benzene (1.5 mL) were degassed in a Teflon screw-capped tube covered by aluminum foil and heated at 150 °C under N_2 for 4 days. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give Rh(ttp)Bn (15 mg, 0.017 mmol, 69%).

At 200 °C. Rh(ttp)Me (20 mg, 0.025 mmol) and toluene (1.5 mL) were degassed in a Teflon-stoppered tube covered by aluminum foil and heated at 200 °C under N_2 for 2 h. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give Rh(ttp)Bn **1c** (20 mg, 0.023 mmol, 91%).

General Procedure for Reactions of Rh(ttp)Me with Toluene and Various Bases. A. Without Base. Rh(ttp)Me (20 mg, 0.025 mmol) and toluene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 6 h with the reaction tube covered by aluminum foil. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give Rh(ttp)Bn **1c** (17 mg, 0.020 mmol, 80%) and recovered Rh(ttp)Me (2.3 mg, 0.003 mmol, 12%).

B. Addition of K_2CO_3. Rh(ttp)Me (20 mg, 0.025 mmol), 10 equiv of K_2CO_3 (35 mg, 0.25 mmol), and toluene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 6 h with the reaction tube covered by aluminum foil. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give Rh(ttp)Bn **1c** (7 mg, 0.0083 mmol, 33%) and recovered Rh(ttp)Me (11 mg, 0.014 mmol, 55%).

C. Addition of K_3PO_4. Rh(ttp)Me (20 mg, 0.025 mmol), 10 equiv of K_3PO_3 (53 mg, 0.25 mmol), and toluene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 6 h with the reaction tube covered by aluminum foil. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give Rh(ttp)Bn **1c** (3 mg, 0.0035 mmol, 14%) and recovered Rh(ttp)Me (14 mg, 0.018 mmol, 72%).

D. Addition of 3 equiv of Ph_3P. Rh(ttp)Me (20 mg, 0.025 mmol), Ph_3P (20 mg, 3 equiv), and toluene (1.5 mL) were degassed in a Teflon-stoppered tube covered by aluminum foil and heated at 150 °C under N_2 for 6 h. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with CH_2Cl_2 to give (Ph_3P)Rh(ttp)Me (14 mg, 0.013 mmol, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz): −6.95 (d, 3H, J = 2.4 Hz), 4.90 (br s, 6 H), 6.73 (t, 6 H, J = 7.2 Hz), 6.98 (t, 3 H, J = 7.2 Hz), 7.48 (d, 8 H, J = 8.2 Hz), 7.73 (d, 4 H, J = 8.5 Hz), 7.94 (d, 4 H, J = 8.4 Hz), 8.59 (s, 8 H).

General Procedure for Reactions of Rh(ttp)Me with Various Substituted Toluenes. Reaction of Rh(ttp)Me with *p*-Xylene. Rh(ttp)Me (20 mg, 0.025 mmol) and *p*-xylene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 7 h with the reaction tube covered by aluminum foil. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give 4-$CH_3C_6H_4CH_2$Rh(ttp) **1a** (17 mg, 0.019 mmol, 76%) as a red solid. R_f = 0.65 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): −3.77 (d, 2 H, J = 3.6 Hz), 1.68 (s, 3 H), 2.70 (s, 12 H), 2.87 (d, 2 H, J = 7.8 Hz), 5.66 (d, 2 H, J = 7.8 Hz), 7.54 (dd, 8 H, J = 2.1, 6.8 Hz), 7.96 (dd, 4 H, J = 2.1, 7.1 Hz), 8.07 (dd, 4 H, J = 2.1, 7.7 Hz), 8.67 (s, 8 H). Calcd for $(C_{56}H_{45}N_4Rh)^+$: *m*/*z* 876.2694; found *m*/*z* 876.2667. Anal. Calcd for $C_{56}H_{45}N_4Rh$: C, 76.70; H, 5.17; N, 6.39. Found: C, 76.64; H, 5.28; N, 6.06.

Reaction of Rh(ttp)Me with 4-*tert*-Butyltoluene. Rh(ttp)Me (20 mg, 0.025 mmol) and 4-*tert*-butyltoluene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 4 h to give 4-^{t}Bu$C_6H_4CH_2$Rh(ttp) **1b** (19 mg, 0.021 mmol, 82%) as a red solid. R_f = 0.75 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): −3.79 (d, 2 H, J = 3.6 Hz), 0.96 (s, 9 H), 2.70 (s, 12 H), 2.93 (d, 2 H, J = 8.1 Hz), 5.89 (d, 2 H, J = 8.4 Hz), 7.54 (t, 8 H, J = 6.0 Hz), 8.04 (t, 8 H, J = 7.9 Hz), 8.65 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 13.00 (d, $^1J_{Rh-C}$ = 26.6 Hz), 21.91, 31.01, 34.48, 122.75, 113.30, 124.47, 127.60, 131.68, 134.13, 134.23, 137.41, 139.76, 143.49, 146.20. Calcd for $(C_{59}H_{51}N_4Rh)^+$: *m*/*z* 918.3163; found *m*/*z* 918.3139. Anal. Calcd for $C_{55}H_{43}N_4Rh$: C, 77.11; H, 5.59; N, 6.09. Found: C, 76.66; H, 5.65; N, 5.91.

Reaction of Rh(ttp)Me with 4-Fluorotoluene. Rh(ttp)Me (20 mg, 0.025 mmol) and 4-fluorotoluene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 15 days to give 4-$FC_6H_4CH_2$Rh(ttp) **1d** (11 mg, 0.012 mmol, 48%) as a red solid. R_f = 0.60 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): −3.83 (d, 2 H, J = 3.9 Hz), 2.70 (s, 12 H), 2.89 (dd, 2 H, J = 2.7, 5.7 Hz,), 5.55 (t, 2 H, J = 8.7 Hz), 7.55 (t, 8 H, J = 6.6 Hz), 7.98 (dd, 4 H, J = 2.1, 8.0 Hz), 8.06 (d, 4 H, J = 1.2, 8.0 Hz), 8.68 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 11.43 (d, $^1J_{Rh-C}$ = 27.3 Hz), 21.89, 112.96 (d, $^1J_{C-F}$ = 20.9 Hz), 122.83, 126.08, 126.18, 127.78, 131.83, 134.16, 134.21, 137.52, 139.61, 143.45. Calcd for $(C_{55}H_{43}N_4Rh)^+$: *m*/*z* 880.2443; found *m*/*z* 880.2426. Anal. Calcd for $C_{55}H_{43}N_4Rh$: C, 74.61; H, 5.07; N, 6.39. Found: C, 74.99; H, 4.81; N, 6.36.

Reaction of Rh(ttp)Me with 4-Chlorotoluene. Rh(ttp)Me (20 mg, 0.025 mmol) and 4-chlorotoluene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 4 days to give 4-$ClC_6H_4CH_2$Rh(ttp) **1e** (15 mg, 0.017 mmol, 69%) as a red solid. R_f = 0.60 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): −3.84 (d, 2 H, J = 3.9 Hz), 2.70 (s, 12 H), 2.89 (d, 2 H, J = 8.4 Hz), 5.58 (d, 2 H, J = 8.4 Hz), 7.55 (t, 8 H, J = 7.2 Hz), 7.96 (dd, 4 H, J = 1.5, 7.1 Hz), 8.06 (dd, 4 H, J = 1.5, 7.1 Hz), 8.69 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 10.67 (d, $^1J_{Rh-C}$ = 27.4 Hz), 21.89, 122.87, 126.23, 126.25, 127.79, 131.90, 134.22, 137.54, 139.56, 140.12, 143.45. Calcd for $(C_{55}H_{42}N_4ClRh)^+$: *m*/*z* 896.2148; found *m*/*z* 896.2138. Anal. Calcd for $C_{55}H_{42}N_4ClRh$: C, 73.62; H, 4.70; N, 6.24. Found: C, 73.21; H, 5.12; N, 6.22.

Reaction of Rh(ttp)Me with 4-Methylbenzotrifluoride. Rh(ttp)Me (20 mg, 0.025 mmol) and 4-methylbenzotrifluoride (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C for 4 days. The red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give 4-$F_3CC_6H_4CH_2$Rh(ttp) **1f** (19 mg, 0.020 mmol, 83%) as a red solid. R_f = 0.60 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): −3.81 (d, 2 H, J = 3.9 Hz), 2.70 (s, 12 H), 2.96 (d, 2 H, J = 8.0 Hz), 6.08 (d, 2 H, J = 8.1 Hz), 7.54 (d, 4 H, J = 7.8 Hz), 7.55 (d, 4 H, J = 7.6 Hz), 7.94 (d, 4 H, J = 8.0 Hz), 8.05 (d, 4 H, J = 8.0 Hz), 8.70 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 9.49 (d, $^1J_{Rh-C}$ = 27.5 Hz), 21.68, 122.73, 122.78, 125.20 (q, $^1J_{C-F}$ = 31.2 Hz), 125.70, 127.60, 131.77, 132.28, 133.70, 137.41, 139.25, 143.24, 145.78. Calcd for $(C_{56}H_{42}N_4F_3Rh)^+$: *m*/*z* 930.2411; found *m*/*z* 930.2391.

Reaction of Rh(ttp)Me with 4-Methylbenzonitrile. Rh(ttp)Me (20 mg, 0.025 mmol) and 4-methylbenzonitrile (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C for 17 days. The red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give 4-$NCC_6H_4CH_2$Rh(ttp) **1g** (16 mg, 0.018 mmol, 71%) as a red solid. R_f = 0.30 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) −3.87 (d, 2 H, J = 3.9 Hz), 2.71 (s, 12 H), 2.90 (d, 2 H, J = 8.4 Hz), 6.11 (d, 2 H, J = 8.1 Hz), 7.57 (t, 8 H, J = 8.4 Hz), 7.93 (dd, 4 H, J = 1.5, 8.3 Hz), 8.03 (dd, 4 H, J = 1.2, 7.7 Hz), 8.90 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz) 9.27 (d, $^1J_{Rh-C}$ = 28.0 Hz), 21.89, 106.25, 120.01, 122.98, 124.92, 127.89, 129.69, 132.04, 134.12, 134.29, 137.32, 139.32, 143.39. Calcd for $(C_{56}H_{42}N_5Rh)^+$: *m*/*z* 887.2490; found *m*/*z* 887.2487.

Reaction of Rh(ttp)Me with *m*-Xylene. Rh(ttp)Me (20 mg, 0.025 mmol) and *m*-xylene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 3 days with the reaction tube covered by aluminum foil. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give 3-$CH_3C_6H_4CH_2$Rh(ttp) **1h** (17 mg, 0.019 mmol, 77%) as a red solid. R_f = 0.65 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): −3.79 (d, J = 3.9 Hz, 2 H), 1.58 (s, 3 H), 2.63 (s, 1 H), 2.64 (s, 1 H), 2.70 (s, 12 H), 2.80 (d, J = 8.1 Hz, 1 H), 5.77 (t, J = 7.7 Hz, 1 H), 6.32 (d, J = 7.8 Hz, 1 H), 7.53 (d, J = 5.7 Hz, 4 H), 7.55 (d, J = 5.7 Hz, 4 H), 8.00 (dd, J = 2.6, 5.9 Hz, 4 H), 8.06 (dd, J = 2.4, 5.1 Hz, 4 H), 8.67 (s, 8 H). Calcd for $(C_{56}H_{45}N_4Rh)^+$: *m*/*z* 876.2694; found *m*/*z* 876.2682. Anal. Calcd for $C_{56}H_{45}N_4Rh$: C, 76.70; H, 5.17; N, 6.39. Found: C, 76.42; H, 5.09; N, 6.37.

Reaction of Rh(ttp)Me with *o*-Xylene. Rh(ttp)Me (20 mg, 0.025 mmol) and *o*-xylene (1.5 mL) were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 4 days with the reaction tube covered by aluminum foil. The solvent was then removed under vacuum, and the red crude mixture was isolated by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1) to give 2-$CH_3C_6H_4$-CH_2Rh(ttp) **1i** (18 mg, 0.020 mmol, 79%) as a red solid. R_f = 0.65 (*n*-hexane/CH_2Cl_2, 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz): −3.57 (d, J = 3.6 Hz, 2 H), −0.91 (s, 3 H), 2.56 (d, J = 7.5 Hz, 1 H), 2.70 (s, 12 H), 5.66 (t, J = 7.5 Hz, 1 H), 5.72 (d, J = 7.8 Hz, 1 H), 6.31 (t, J = 7.2 Hz, 1 H), 7.53 (d, J = 3.3 Hz, 4 H), 7.54 (d, J = 1.8 Hz, 4 H), 7.96 (dd, J = 1.7, 7.7 Hz, 4 H), 8.05 (dd, J = 2.1, 7.4 Hz, 4 H), 8.67 (s, 8 H). Calcd for $(C_{56}H_{45}N_4Rh)^+$: *m*/*z* 876.2694; found *m*/*z* 876.2703. Anal. Calcd for $C_{56}H_{45}N_4Rh$: C, 76.70; H, 5.17; N, 6.39. Found: C, 76.60; H, 5.11; N, 6.33.

Temperature-Dependent Isotope Effect with Rh(ttp)Me. Kinetic Isotope Effect at 150 °C. Rh(ttp)Me (20 mg, 0.025 mmol) and a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.5 mL) were degassed for three freeze−thaw−pump cycles in the rota-flo tube. The tube was covered by aluminum foil and heated to 150 °C under N_2 for 1 d. The isotope ratio of Rh(ttp)Bn to Rh(ttp)Bn-d_7 was determined to be 2.7 by integration of ^{1}H NMR. (The integration of benzylic protons (1.470) was used to calculate the ratio with the integration of pyrrole signal set as 8.000). The results were the average of at least two runs.

Kinetic Isotope Effect at 200 °C. Rh(ttp)Me (20 mg, 0.025 mmol), a premixed equimolar solvent mixture of toluene/toluene-d_8 (1.5 mL) were degassed for three freeze−thaw−pump cycles in a RotaFlo tube. The tube was covered by aluminum foil and heated to 200 °C under N_2 for 2.5 h. The isotope ratio of Rh(ttp)Bn to Rh(ttp)Bn-d_7 was determined to be 2.8 by integration of ^{1}H NMR. (The integration of benzylic protons (1.475) was used to calculate the ratio with the integration of the pyrrole signal set as 8.000.) The results were the average of at least two runs.

Attempted H/D Exchange. Rh(ttp)Bn (10 mg, 0.012 mmol) and toluene-d_8 (1.5 mL) were degassed for three freeze−thaw−pump cycles and then heated at 200 °C under N_2 for 2.5 h to give only recovered Rh(ttp)Bn (9.2 mg, 0.0107 mmol, 92%).

Competition Experiments of 4-Substituted Toluene. Rh(ttp)Me (10 mg, 0.013 mmol), a premixed equimolar solvent mixture of toluene (13.5 μL, 0.13 mmol), and *p*-xylene (16 μL, 0.13 mmol) in benzene (1.5 mL) as the solvent were degassed for three freeze−thaw−pump cycles and heated at 150 °C under N_2 for 3 days in a Teflon-stoppered tube. After the reaction was complete, the ^{1}H NMR spectrum of the crude reaction mixture was taken. The ratio of $k(H_{FG}/H_H)$ was calculated from the ratio of the benzylic protons with reference to the pyrrole proton in the ^{1}H NMR spectrum from at least two runs. A series of experiments was carried out using various functionalized toluenes, i.e., 4-*tert*-butyltoluene (22 μL, 0.13 mmol), 4-fluorotoluene (14 μL, 0.13 mmol), 4-chlorotoluene (15 μL, 0.13 mmol), and 4-methylbenzotrifluoride (18 μL, 0.13 mmol). The ratios of $k(H_{FG}/H_H)$ were calculated from the integration of the benzylic protons in the ^{1}H NMR spectra. The results were the average of at least two runs of experiments.

Attempted Exchange. Rh(ttp)Bn (10.0 mg, 0.012 mmol) and 4-*tert*-butyltoluene (1.5 mL) were degassed for three freeze−thaw−pump cycles and then heated at 150 °C under N_2 for 1 day to give only Rh(ttp)Bn (9.0 mg, 0.0104 mmol, 90%).

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Supporting Information Available: Text, tables, and figures of crystallographic data for complexes **1b** and **1d** (CIF and PDF), ^{1}H and ^{13}C NMR spectra for **1f** and **1g**. This material is available free of charge via the Internet at http://pubs.acs.org.